

AD-A085 960

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THE SYNTHESIS AND REACTIONS OF 2,4-DITERTIARYBUTYL-3-CHLORO-1-L-ETC(U)

JUN 80 A H COWLEY, S K MEHROTRA, H W ROESKY

N00014-76-C-0577

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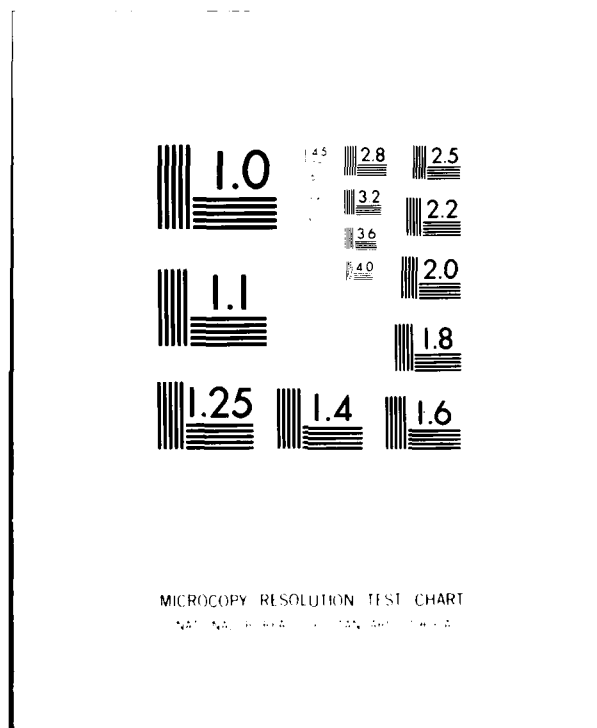
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LEVEL II b.s (12)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER

80-01

2. GOVT ACCESSION NO.

AD-A085960

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

The Synthesis and Reactions of 2,4-Ditertiarybutyl-
3-Chloro-1- λ^6 -Thia-2,4-Diaza-3-Phosphetidine-1,1-
Dioxide, A Heterocycle Containing Nitrogen, Sul-
fur, and Tricoordinate Phosphorus

5. TYPE OF REPORT & PERIOD COVERED

Technical Report 1980

6. PERFORMING ORG. REPORT NUMBER

TR 80-01 ✓

7. AUTHOR(s)

Alan H. Cowley,* Sushil K. Mehrotra, and
Herbert W. Roesky*

8. CONTRACT OR GRANT NUMBER(s)

N00014-76-C-0577 ✓

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Chemistry ✓
University of Texas at Austin
Austin, Texas 78712

10. PROGRAM ELEMENT, PROJECT, TASK
AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

Office of Naval Research
Department of the Navy

12. REPORT DATE

JUNE 16, 1980

13. NUMBER OF PAGES

22

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING
SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for Publication in Inorganic Chemistry

18. SUPPLEMENTARY NOTES

DTIC
ELECTE
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Four-membered sulfur-nitrogen-phosphorus (thiadiazaphosphetidine) ring
Metathetical reactions
Iron tetracarbonyl complex
 ^1H , ^{13}C , ^{31}P NMR data

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A new four-membered nitrogen-sulfur-phosphorus ring of composition
 $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCl}$ has been prepared by the action of PCl_3 on the sulfamide,
 $(\text{t-BuNH})_2\text{SO}_2$ in the presence of Et_3N and characterized by elemental
analysis, and NMR, IR, and mass spectroscopy. Reaction of the title

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EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

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compound with SbF_3 and $\text{Me}_3\text{SiNMe}_2$ afforded the 3-fluoro and 3-dimethylamino derivatives, $\text{O}_2\text{S}(\text{t-BuN})_2\text{PF}$ and $\text{O}_2\text{S}(\text{t-BuN})_2\text{PNMe}$, respectively, and treatment with sodium in *n*-octane produced the diphosphine, $[\text{O}_2\text{S}(\text{t-BuN})_2\text{P}]_2$. Treatment of the thiadiazaphosphetidine ring with $\text{Fe}_2(\text{CO})_9$ afforded the phosphorus-iron bonded complex, $\text{O}_2\text{S}(\text{t-BuN})_2\text{P}(\text{Cl})\text{Fe}(\text{CO})_4$.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

OFFICE OF NAVAL RESEARCH

(15) Contract N00014-76-C-0577

Task No. NR 053-612

(9) TECHNICAL REPORT NO. 80-01

(14) TR-80-01

(6) THE SYNTHESIS AND REACTIONS OF 2,4-DITERTIARYBUTYL-3-CHLORO-1-Lambda π^6 -THIA-2,4-DIAZA-3-PHOSPHETIDINE-1,1-DIOXIDE, A HETEROCYCLE CONTAINING NITROGEN, SULFUR, AND TRICOORDINATE PHOSPHORUS.

(10) Alan H./Cowley Sushil K./Mehrotra
Herbert W./Roesky

Prepared for Publication

in

INORGANIC CHEMISTRY

Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

(11) 16 Jun 1980

Accession For	
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(12) 27

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Contribution from the Department
of Chemistry, University of Texas at
Austin, Austin, Texas 78712, and the
Anorganisch-Chemisches Institut der
Universität, Frankfurt/Main,
Niederurseler Hang, D-6000 Frankfurt/
Main 50, W. Germany

THE SYNTHESIS AND REACTIONS OF 2,4-DITERTIARYBUTYL-3-CHLORO-1- λ⁶-THIA-2,4-DIAZA-3-PHOSPHETIDINE-1,1-DIOXIDE, A HETEROCYCLE CONTAINING NITROGEN, SULFUR, AND TRICOORDINATE PHOSPHORUS

ALAN H. COWLEY^{1*}, SUSHIL K. MEHROTRA¹, and HERBERT W. ROESKY^{2*}

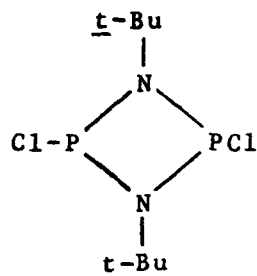
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A new four-membered nitrogen-sulfur-phosphorus ring
of composition $O_2S(t-BuN)_2PCl$ has been prepared by the
action of PCl_3 on the sulfamide, $(t-BuNH)_2SO_2$ in the
presence of Et_3N and characterized by elemental analysis,
and NMR, IR, and mass spectroscopy. Reaction of the
title compound with SbF_3 and Me_3SiNMe_2 afforded the 3-
fluoro and 3-dimethylamino derivatives, $O_2S(t-BuN)_2PF$
and $O_2S(t-BuN)_2PNMe$, respectively, and treatment with
sodium in n-octane produced the diphosphine,
 $\{O_2S(t-BuN)_2P\}_2$. Treatment of the thiadiazaphosphetidine
ring with $Fe_2(CO)_9$ afforded the phosphorus-iron bonded
complex, $O_2S(t-BuN)_2P(Cl)Fe(CO)_4$.

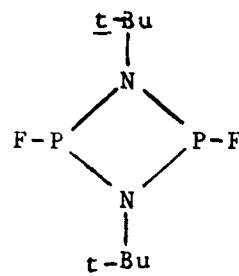
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INTRODUCTION

Following the discovery of the diazadiphosphetidines **1A**^{3,4} and **1B**,⁵ numerous publications have appeared concerning

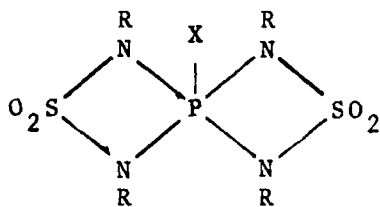


1A



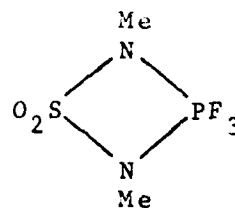
1B

the stereochemistry,⁶ ligative behavior,⁷ and cognate chemistry⁸ of this class of compound. The present paper is concerned with the synthesis of a four-membered nitrogen-sulfur-phosphorus ring system, which is related to the dihalodiphosphetidines by replacing a PX by an SO₂ moiety. This particular four-membered (thiadiazaphosphetidine) ring system has, in fact, been known for a number of years. For example, Becke-Goehring and co-workers⁹ prepared the pentacoordinate phosphorus compounds 2-5.

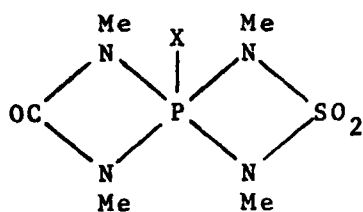


X = F, Cl
R = Me, Ph

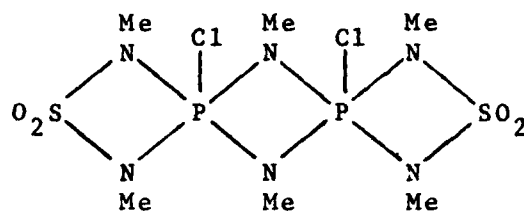
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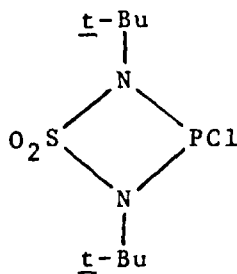
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More recently, it has been shown that the reaction of N,N'-dimethyl- or N,N'-diethylsulfamide with PCl_3 in the presence of tertiary amines leads to apparently polymeric materials of composition $[\text{O}_2\text{S}(\text{NMe})_2\text{PCl}]_n$ and to ring-opened products, respectively.¹⁰

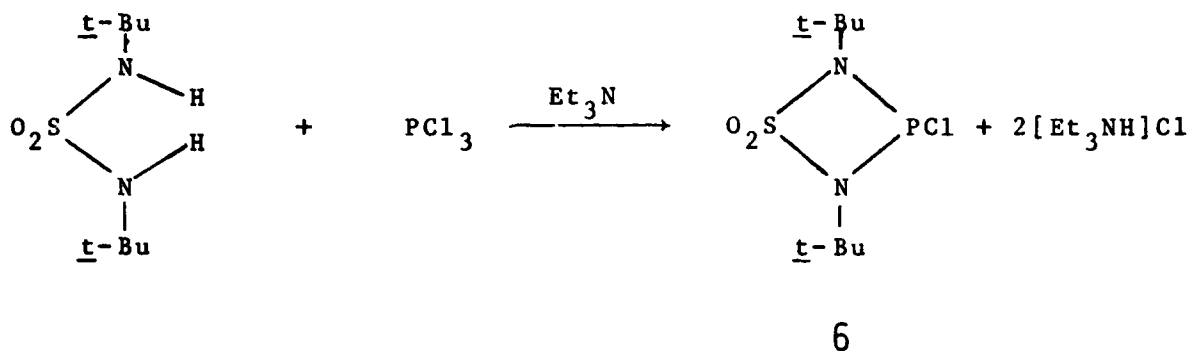
Since it is known from e.g. diazadiphosphetidine chemistry that sterically bulky nitrogen substituents stabilize the four-membered ring, we decided to investigate the reaction of N,N'-ditertiarybutylsulfamide with PCl_3 in an effort to prepare 6.



6

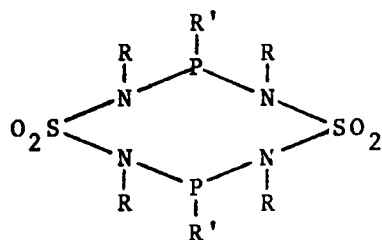
RESULTS AND DISCUSSION

2,4-ditertiarybutyl-3-chloro-1- λ^6 -thia-2,4-diaza-3-phosphetidine-1,1-dioxide, **6**, can be prepared by the action of PCl_3 on the sulfamide, $(\text{t-BuNH})_2\text{SO}_2$ in the presence of Et_3N .



The monomeric nature of **6** is indicated by the mass spectrum which exhibits a parent peak at m/e 273. There was no evidence for species possessing higher mass.

The significance of **6** is that it represents the first example of a four-membered nitrogen-sulfur-phosphorus (III) ring. As pointed out in the Introduction, only pentacoordinate phosphorus compounds featuring this ring system had been described previously.⁹ The successful synthesis of **6** can be attributed to the steric demands of the *t*-butyl groups since the attempted syntheses of the methyl or ethyl analogues of **6** resulted in production of apparently polymeric substances of composition, $[\text{O}_2\text{S}(\text{NMe})_2\text{PCl}]_n$, or to ring-opened products.¹⁰ Replacement of PCl_3 by the phosphinous chlorides, MePCl_2 or PCl_3 , resulted in the production of eight-membered ring compounds, **7**.¹⁰



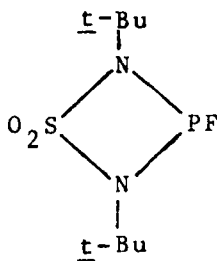
R' = Me, Ph

R = Me, Et

7

The geometry of **6**, by analogy with that of the diazadipho-phetidine, **1A**⁶, is expected to feature a slightly puckered four-membered ring with both nitrogens possessing essentially trigonal planar geometries. Moreover, since the SO₂ moiety of **7** is arranged with the O-S-O planes perpendicular to the N-S-N planes,¹⁰ a similar structural feature may be assumed for **6**. With these assumptions it is obvious that **6** can exist in only one conformation. Accordingly, only one peak was detectable in the ³¹P NMR (Table I).

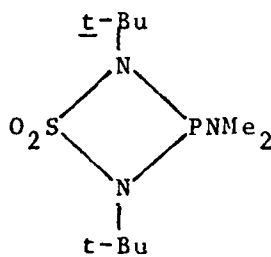
Treatment of **6** with SbF₃ and a catalytic amount of SbF₅ affords **8** in ~69% yield. Conventional elemental analysis (Table II) of **8**



8

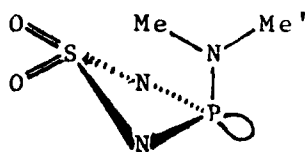
proved to be very difficult due to the moisture sensitivity of the compound. Accordingly, the characterization of **8** was based on NMR and mass spectroscopy. For example, a parent peak is apparent in the mass spectrum of **8** at m/e 256. Moreover, the presence of a PF (rather than e.g. a PF_3) moiety is established by the ^{31}P and ^{19}F NMR spectra of **8**, both of which consist of doublet at anticipated chemical shift values (Table I).

The metathetical reaction of **6** with Me_3SiNMe_2 affords **9** in virtually quantitative yield.



9

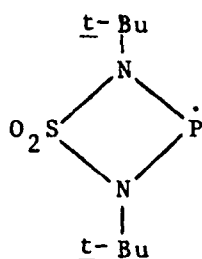
Compound **9** is a fluxional molecule. Below $-40^{\circ}C$ two N-methyl signals are apparent in the 1H NMR spectrum (Figure 1). Coalescence occurs $\sim 40^{\circ}C$, and above this temperature averaging of the two methyl environments becomes rapid on the NMR time scale. The foregoing observations can be accommodated by postulating **10** as the ground state structure. In this conformation one of the exocyclic N-methyl groups (Me') is situated syn to the phosphorus lone pair while the other (Me) lies across the PN_2S ring.



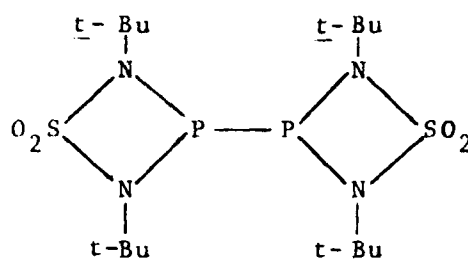
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Assignment of the larger PNCH coupling to Me' (Table I) is consistent with previous observations on aminophosphines¹¹ and with more general trends concerning the influence of a syn lone pair of electrons on coupling constants.¹² A parallel may be drawn between 10 and the ground state structure which has been suggested¹³ for R₂N-substituted diazaphospholanes. We note that other suggestions have been made¹⁴ for the geometry of the exocyclic R₂N moiety in diazaphospholanes. However, we favor 10 because it corresponds to the "bisected" geometry of acyclic aminophosphines¹⁵ in which the nitrogen and phosphorus lone pairs are mutually orthogonal.

Lappert, Goldwhite, and co-workers¹⁶ have shown that the treatment of phosphinous chlorides with sodium or electron-rich-olefins leads to the production of stable radicals, R₂ \dot{P} , provided the bulk of the R groups is sufficient to impart kinetic stabilization. We were therefore prompted to treat 6 with sodium in n-octane in an attempt to generate 11. However, 11 is not sufficiently long-lived to permit its isolation or spectroscopic identification and the reaction results in the production of the diphosphine 12 which is the dimer of 11.



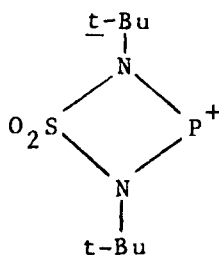
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12

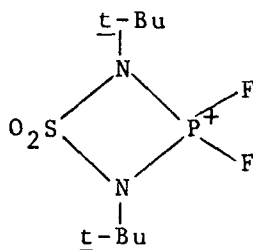
The conformational behavior of diphosphines is a matter of current interest. On one hand, it has been found that the gauche ground state preference of tetraalkyldiphosphines increases as the steric bulk of the alkyl group is increased from Me to t-Bu.¹⁷ On the other hand, we have found recently that bulky aryl groups, such as mesityl, favor the adoption of the anti conformation.¹⁸ In the case of 12, the ¹H NMR signal for the t-Bu groups remains a singlet down to -90°C. In all likelihood, P-P rotation is still rapid on the NMR time scale at this temperature; however, our observations are also consistent with an anti ground state geometry.

The treatment of haloaminophosphines with halide ion abstractors has been shown¹⁹ to result in amino-substituted phosphonium ions, R₂P⁺. We therefore attempted to prepare 13 via



13

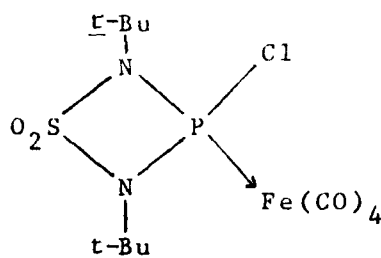
the following routes: (1) the reaction of 6 with Al_2Cl_6 , (2) the reaction of 6 with NaBPh_4 , (3) the reaction of 6 with AgBF_4 , and (4) the reaction of 8 with SbF_5 . Reactions 1 and 2 do not proceed, reaction 3 affords $\text{O}_2\text{S}(\text{t-BuN})_2\text{PF}$ (8) and unidentified products, while reaction 4 produces the phosphonium cation 14,



14

together with unidentified products. Reaction 4 implies the net transfer of F^+ from SbF_5 to 8.²⁰ While the mechanism of this reaction is unknown, it can be speculated that two steps are involved. Presumably, the first step involves oxidative fluorination of 8 to the trifluorophosphorane, and the second step is fluoride ion abstraction from the latter.

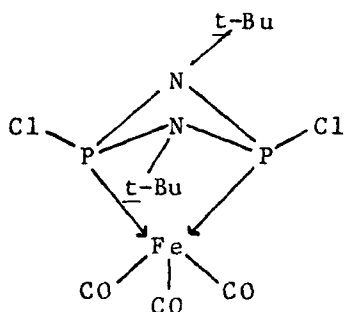
From the reaction of 6 with $\text{Fe}_2(\text{CO})_9$ it is possible to isolate 15 in almost quantitative yield.



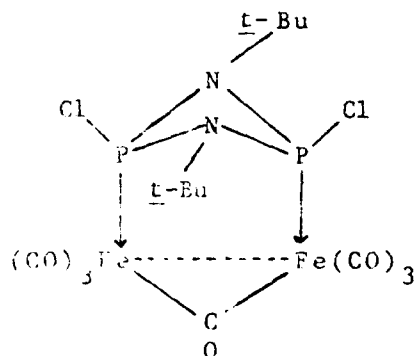
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This compound is formulated as the P-bonded complex for the following reasons: (i) there is a significant change in the ^{31}P NMR chemical shift upon coordination (Table II); (ii) coupling between ^{31}P and the carbonyl carbons is detectable and of appropriate magnitude for $^2J_{\text{PFeC}}$; and (iii) ^{13}C NMR spectroscopy indicates that the t-Bu groups are isochronous.

It is interesting to contrast the behavior of **1A** and **6** toward $\text{Fe}_2(\text{CO})_9$. The diazadiphosphetidine, **1A**, can act in a chelating (**16**) or bridging (**17**) capacity.^{7a,c}



16



17

Finally, we note that although the phosphorus atom of 6 can behave as a donor toward an $\text{Fe}(\text{CO})_4$ moiety, it is not sufficiently active to react with elemental sulfur or MeI .

EXPERIMENTAL SECTION

MATERIALS AND GENERAL PROCEDURES. N,N' -ditertiarybutylsulfamide, $\text{O}_2\text{S}(\text{t-BuNH})_2$ was prepared according to the method of Bermann and Van Wazer.²¹ The physical properties of $\text{O}_2\text{S}(\text{t-BuNH})_2$ corresponded to those reported by Stowell.²² Dimethylamino-trimethylsilane was synthesized by the literature method²³, and $\text{Fe}_2(\text{CO})_9$ was prepared by UV irradiation of $\text{Fe}(\text{CO})_5$ in n -pentane. All other reagents were procured commercially and used without subsequent purification. All solvents were carefully dried prior to use.

Virtually all the materials described herein are moisture sensitive. Accordingly, it was necessary to perform all operations in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada. The analytical data are summarized in Table II.

SPECTROSCOPIC MEASUREMENTS. The ^1H and ^{19}F NMR spectra were recorded on Varian A-60 and EM-390 instruments operating at spectrometer frequencies of 60 and 84.96 MHz, respectively. The variable temperature ^1H NMR experiments were conducted on a Varian HA 100 spectrometer. Except where indicated in Table I,

the ^1H and ^{19}F chemical shifts were measured with respect to internal CH_2Cl_2 (δ , 5.28 ppm) relative to Me_4Si and external CCl_3F , respectively. The ^{13}C and ^{31}P NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at spectrometer frequencies of 22.6 and 30.6 MHz, respectively. Dichloromethane (54.2 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra. The NMR data are summarized in Table I.

IR spectra of nujol mulls were recorded on a Perkin-Elmer 137 spectrophotometer using NaCl plates. Selected IR data are summarized in Table I. The mass spectra were determined on a CEC 21-491 spectrometer at an ionizing voltage of 70 eV.

PREPARATION OF $\text{O}_2\text{S}(\text{t-Bu})_2\text{PCL}$ (6). A 20% excess of the required amount of Et_3N was added to a solution of 6.0g (28.8 mmol) of $\text{O}_2\text{S}(\text{t-BuNH})_2$ in ~60 mL diethyl ether. To this solution, a solution of 3.8g (27.7 mmol) of PCl_3 in 15 mL of Et_2O was added slowly with constant stirring. An exothermic reaction was observed. After the addition was complete, the mixture was refluxed for approximately 4h. Filtration, removal of solvent, and subsequent vacuum distillation (bp 86-91°C @ 0.5 torr) gave an oil which solidified immediately upon cooling. The yield of the product after distillation was 5.0g (18.3 mmol, 64.7% yield). The white solid, mp 61-4°C, can also be purified by sublimation in vacuo or by recrystallization from a mixture of dichloromethane and n-pentane at low temperatures.

PREPARATION OF $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PF}$ (8). A mixture of 6.44g (24.4 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCl}$, a 20% excess of SbF_3 , and a catalytic amount of SbF_5 in ~60 mL of dichloromethane was refluxed for approximately 6h. Filtration and removal of solvent gave a white, solid product which contained some impurities. Purification was achieved by vacuum distillation at 81°C (0.5 torr). A white crystalline solid, mp $53\text{-}5^\circ\text{C}$, was formed on cooling. The yield was 69% (4.3g, 16.78 mmol).

PREPARATION OF $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PNMe}_2$ (9). A solution of 2.0g (7.33 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCl}$ (6) and 0.94g (8.02 mmol) of $\text{Me}_3\text{SiNMe}_2$ in ~40 mL of CH_2Cl_2 was stirred at -20°C for 2h. The temperature of the reaction mixture was raised slowly, initially to room temperature and then to reflux. The refluxing was continued for 2h. Removal of solvent and subsequent vacuum distillation ($86\text{-}87^\circ\text{C}$ at 0.5 torr) gave the pure white, waxy solid product in 96% yield (1.98g, 7.04 mmol).

PREPARATION OF $[\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{P}]_2$ (12). A mixture of 3.48g (12.8 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCl}$ (6) and 0.43g (18.7 mmol) of Na in 40 mL of n-octane was heated under reflux for 3h. A black solid separated out from the reaction mixture as the sodium reacted. Filtration and removal of the solvent gave 2.34g (4.95 mmol) of yellowish solid 12.

ATTEMPTED PREPARATION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{P}^+\text{I}^-$ (13)

ATTEMPTED REACTION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) WITH Al_2Cl_6 .

Aluminum trichloride (1.5g, 1.13 mmol) was added to a stirred solution of 3.1g (1.14 mmol) of $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) at -80°C . The suspended solid dissolved slowly; however, ^{31}P NMR spectroscopic assay of the solution revealed only the presence of unreacted 6.

ATTEMPTED REACTION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) WITH $\text{NaB}\phi_4$.

Sodium tetraphenylborate (2.495g, 7.29 mmol) was added to a solution of 6 (1.99g, 7.30 mmol) in ~30 mL of CH_2Cl_2 at -80°C . The mixture was stirred for 2h at this temperature, allowed to warm to room temperature, and stirred an additional 4h. ^{31}P NMR spectroscopic assay of the solution indicated that no reaction had occurred.

REACTION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) WITH AgBF_4 . Silver tetrafluoroborate (2.31g, 1.19 mmol) was added to a stirred solution of 2.3g (0.84 mmol) of $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) in ~20 mL of CH_2Cl_2 at -80°C . An evolution of gas was observed at low temperatures. The ^{31}P NMR spectrum of the solution at room temperature revealed the presence of $\text{O}_2\text{S}(\text{t-BuN})_2\text{PF}$ (8) together with some unidentified signals.

REACTION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{PF}$ (8) WITH SbF_5 . Antimony pentafluoride (3.6g, 1.66 mmol) was added to a vigorously stirred

solution of 4.23g (1.65 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PF}$ (8) in ~20 mL of CH_2Cl_2 at -80°C . The ^{31}P spectrum of the solution was measured after approximately 3h of stirring, and found to consist of several peaks. The color of the solution changed from colorless to black during this time. After 2 days, the ^{31}P spectrum of the reaction mixture exhibited a triplet at 31.98 ppm with $J_{\text{PF}} = 1187.4$ Hz, which is attributed to the difluorophosphonium cation, $[\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PF}_2]^+$.

PREPARATION OF $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{P}(\text{CL})\text{Fe}(\text{CO})_4$ (15). A mixture of 1.95g (7.15 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCl}$ and 2.2g (6.05 mmol) of Fe_2CO_9 in ~30 mL of n-pentane was heated under reflux for 4-5h. The suspended solid went into solution slowly accompanied by the evolution of gas and change of color of the reaction mixture from yellow to brown. After stripping the solvent, the product was evacuated for 4 h, then recrystallized from n-pentane at low temperatures. Yellow needles of 15 (mp $123-4^\circ\text{C}$) were obtained in virtually quantitative yield.

ATTEMPTED REACTION OF $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCL}$ (6) WITH MeI . A solution of 1.2g (0.44 mmol) of $\text{O}_2\text{S}(\underline{\text{t}}\text{-BuN})_2\text{PCl}$ (6) and ~15 mL of MeI was heated under reflux for approximately 5h. The solution remained clear during this period. ^{31}P NMR spectroscopy indicated the presence of only unchanged starting material.

ATTEMPTED REACTION OF $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) WITH ELEMENTAL SULFUR. A mixture of 2.63g (0.96 mmol) of $\text{O}_2\text{S}(\text{t-BuN})_2\text{PCL}$ (6) and an excess of elemental sulfur was refluxed in benzene for approximately 5h. Upon standing overnight, yellow crystals of elemental sulfur deposited from the solution. NMR spectroscopic examination of the filtrate revealed only the presence of unchanged starting material.

ACKNOWLEDGEMENT. The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612), the Deutschen Forschungsgemeinschaft, dem Fonds der Chemischen Industrie and Hoechst AG for generous financial support.

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TABLE I. Summary of NMR Data for Thiadiazaphosphetidines

compd	Chemical Shifts (ppm) ^a				Coupling Constants (Hz)
	¹ H	¹³ C	¹⁹ F	³¹ P	
O ₂ S(<u>t</u> -BuN) ₂ PCl (6)	1.42	29.75 (<u>Me</u> ₃ C)	--	107.43	² J _{PNC} , 2.96; ³ J _{PNCC} , 5.88
		58.49 (<u>Me</u> ₃ C)	--		
O ₂ S(<u>t</u> -BuN) ₂ PF (8)	1.46	30.12 (<u>Me</u> ₃ C)	-58.76	89.46	² J _{PNC} , 5.0; ³ J _{PNCC} , 4.8; ¹ J _{PF} , 1227.5
		57.71 (<u>Me</u> ₃ C)			
O ₂ S(<u>t</u> -BuN) ₂ PNMe ₂ (9)	1.32 Me ₃ C 80°C	29.49 (<u>Me</u> ₃ C)	--	68.44	² J _{PNC} , 8.2; ³ J _{PNCC} , 4.4
	2.65 Me ₂ N 80°C -40°C	55.23 (<u>Me</u> ₃ C)			J _{PNCH} , ⁹
		30.13 (N-Me)			J _{PNCH} , 15; J _{PNCH} , 3
[O ₂ S(<u>t</u> -BuN) ₂ P] ₂ (12)	1.43	29.93 (<u>Me</u> ₃ C)	--	76.87	² J _{PNC} , -0; ³ J _{PNCC} , 3.4;
		57.37 (<u>Me</u> ₃ C)			
O ₂ S(<u>t</u> -BuN) ₂ P(Cl)Fe(CO) ₄ (15)	1.49 ^b	29.34 (<u>Me</u> ₃ C) ^c	--	125.30	² J _{PNC} , -0; ³ J _{PNCC} , 4.4;
		60.26 (<u>Me</u> ₃ C) ^c			² J _{PFeC} , 8.83
		212.21 (CO) ^c			

^a See Experimental Section for statement of references used.

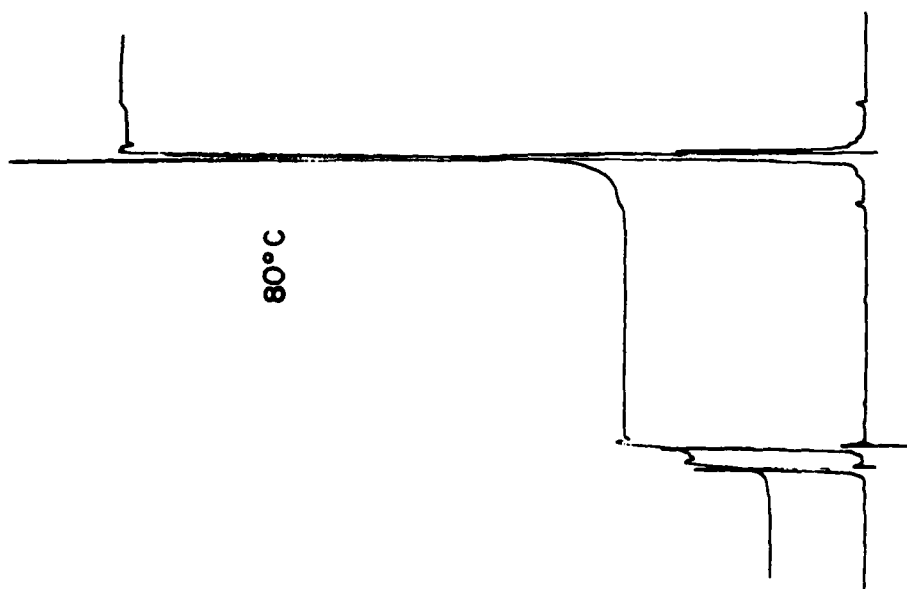
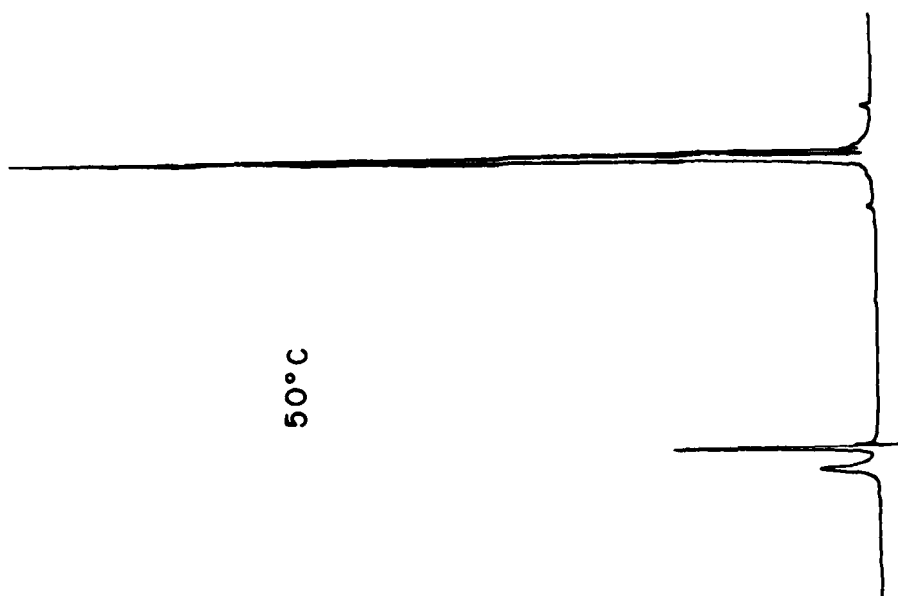
^b Chemical shift measured relative to internal C₆H₆ (δ, 7.24 ppm).

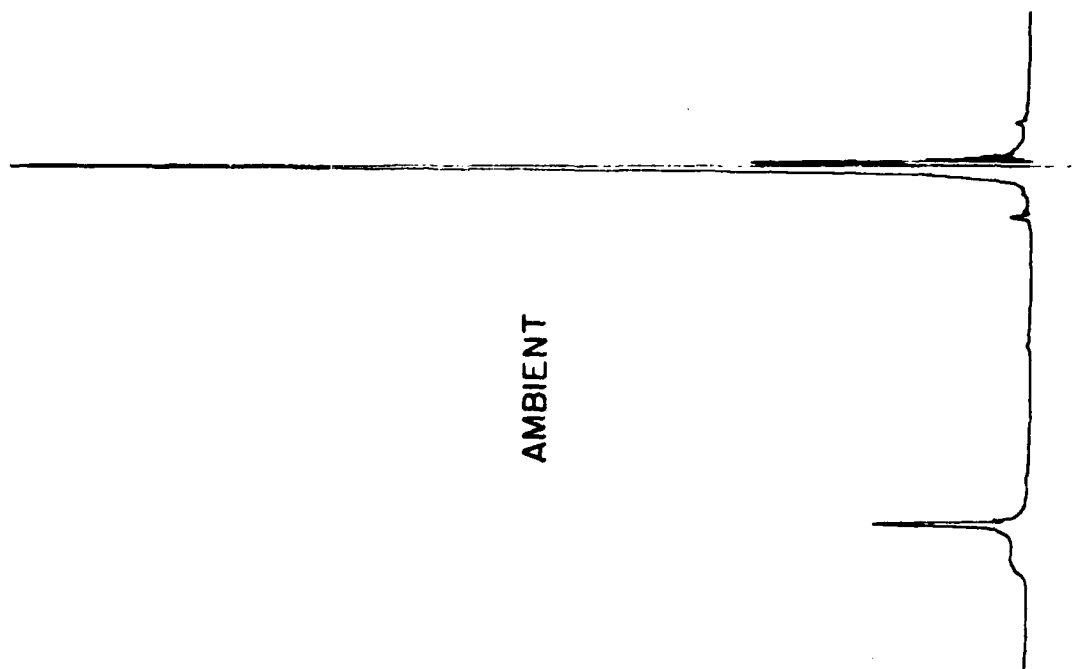
^c Chemical shift measured relative to internal n-pentane (13.70 ppm for Me groups).

TABLE II. Analytical and Infrared Spectroscopic Data for Thiadiazaphosphetidines

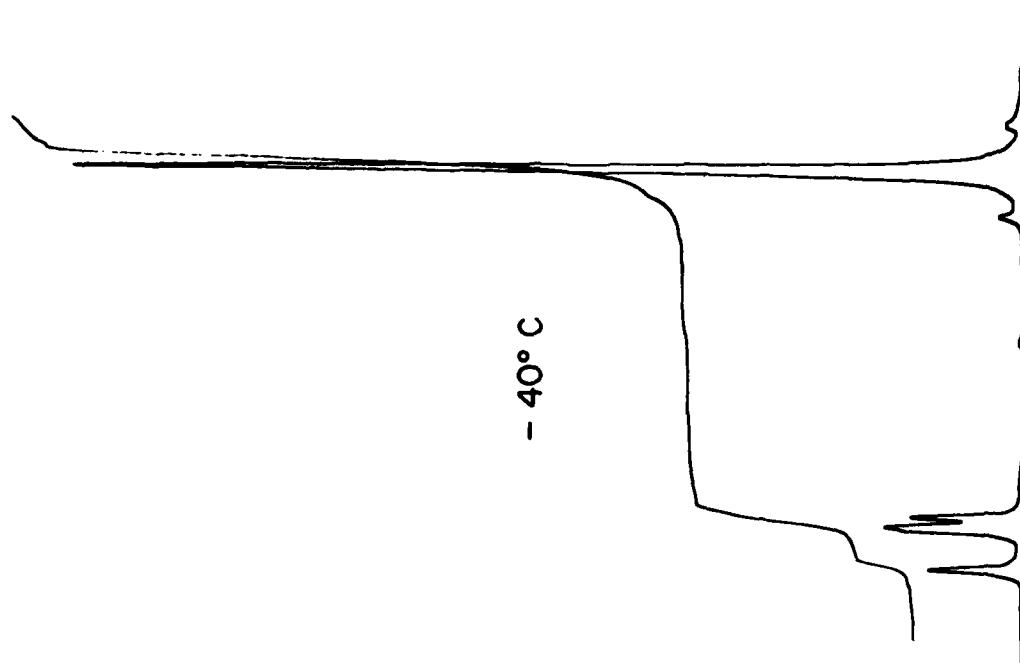
compd	% C		% H		% N		% Cl		IR ^a	
	calcd	found	calcd	found	calcd	found	calcd	found	SO ₂ vibrations ^b	NSN vibrations
O ₂ S(t-BuN) ₂ PCl (6)	35.5	35.3	6.7	6.8	10.3	10.3	13.0	14.5	565, 1178, 1330	893
O ₂ S(t-BuN) ₂ PF (8) ^c	--	--	--	--	--	--	--	--	570, 1170, 1295	902
O ₂ S(t-BuN) ₂ PNMe ₂ (9)	42.7	42.9	8.6	8.9	14.9	14.8	--	--	570, 1168, 1300	890
[O ₂ S(t-BuN) ₂ PI] ₂ (12)	40.5	39.7	7.7	8.3	11.8	11.4	--	--	570, 1170, 1315	905
O ₂ S(t-BuN) ₂ P(Cl)Fe(CO) ₄ (15)	32.7	32.6	4.1	4.4	6.4	6.5	8.1	8.2	528, 1177, 1326	892

^a In cm⁻¹.^b Assigned by analogy to the sulfamide, (t-BuNH)₂SO₂, which exhibits these vibrations at 531, 1140, and 1306 cm⁻¹.^c Analysis impossible due to rapid hydrolysis. See text.





AMBIENT



- 40° C

FIGURE CAPTIONS

FIGURE 1. ^1H NMR spectra of $\text{O}_2\text{S}(\text{t-BuN})_2\text{PNMe}_2$ (9) at various temperatures.

